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OBSERVATIONS AND THOUGHTS ON THE PERFORMANCE OF POLYPROPYLENE GEOMEMBRANE LINERS AND FLOATING COVERS: TOWARDS IMPROVED SPECIFICATIONS

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Abstract: In 2004 the Geosynthetic Research Institute (GRI) temporarily withdrew standard GM 18 because of a number of premature cracking failures in PP liners and floating covers. These field events were very similar to the initial stress cracking failures that occurred in high density polyethylene (HDPE) geomembranes in the early 1980s so should not be viewed as being insurmountable. Failures have occurred in welds, along the edges of welds, in unreinforced panels, at floor/wall wrinkles in tanks, on the top edges and in the troughs of floating covers, at protrusions, on the top layer of reinforced flexible polypropylene (fPP-R) in floating covers, in the bottom layer, through both layers, and even in the container during delivery to site. Cracking has occurred in material exposed to ultra violet (UV) light, not exposed to UV light, exposed and not exposed to chlorinated water, and over a wide range of temperatures. Eight to ten years appears to be a critical exposure period. On the other hand an fPP-R exposed landfill cap shows no degradation after almost 11 years.

All breaks appear to be stress cracks. Repairs are difficult, if not impossible, to make due to the inability of the patch material to bond to the damaged material. It appears to be a failure of the additive packages to provide protection against a synergistic combination of stress and environmental conditions. Opinions on the causes of the failures will be presented. The objective is to develop better PP geomembrane specifications.

Keywords: polypropylene, geomembrane, stress crack, liner, floating cover, OIT tests

INTRODUCTION

Polypropylene (PP) geomembranes were first introduced as Santoprene in the late 1980s, one of the first applications being in pulp mill black liquor ponds in which the associated detergents had previously caused environmental stress cracking failures in some HDPE liners.

Then, in the early 1990s, Himont started to develop PP specifically for geomembrane applications. The resin was made by the Catalloy process in which PP and ethylene propylene rubber (EPR) are catalyzed in-reactor to generate resin pellets consisting essentially of spherical homogeneously integrated layers of PP and EPR.

Both the unreinforced flexible PP (fPP) and reinforced flexible PP (fPP-R) geomembranes were well accepted by geomembrane manufacturers and installers. As a member of the same polyolefin polymer family as polyethylene (PE), PP could be used exposed and covered. It was more flexible and had longer tensile break elongation than linear low density polyethylene (LLDPE), and it had a low coefficient of thermal expansion that generated fewer expansion wrinkles than high density PE (HDPE) in the field. It had a relatively high friction angle, a wide welding window, and was either welded or not welded – there was not a wide grey area of weld quality. Unlike HDPE, but as with LLDPE, it was not susceptible to stress cracking in the as-manufactured condition

Initially the resin was provided with or without an anti-oxidation (AO) and UV resistance stabilization package. Many geomembrane manufacturers chose to add their own packages or even to augment those provided by the resin manufacturer. Both fPP-R and fPP geomembranes were rapidly used for lining potable water tanks, potable water reservoirs, black liquor ponds, irrigation ponds, aquaculture ponds, and at least one solar power pond. They were used as an exposed geomembrane cap (EGC) on a municipal solid waste landfill cap and as floating covers on potable water reservoirs, swimming pools, waste water anaerobic digesters, and landfill leachate lagoons. They worked very well.

Then unexpected longer term performance problems started to occur, much as the slow crack growth (SCG), but not as significantly as the rapid crack propagation (RCP) stress cracking (SC) problems that occurred in HDPE geomembranes in the 1980s and early 1990s. And the problems again appeared to be SC, but now in a material that, due its low crystallinity (~5%), was, unlike HDPE, not susceptible to SC in the as-manufactured condition.

The first failure (Shah 1997) occurred in a solar power pond (strong hot brine solutions) after only 15 months in service. Craze cracking occurred throughout the liner. The cause was traced to the use of a stabilization package designed for HDPE that was thought would also be appropriate for PP since both were members of the polyolefin family. This was not the case. The additive formulation was changed to the one that should have been used in the first place, the liner replaced, and it worked satisfactorily for 6 years until the pond was de-commissioned in 2004. Retained samples removed from the exposed tops of the slopes, through the acidic (pH as low as 2, but typically 3.5) layers, down through the concentrated brine solution at the bottom are still (Reamers 2008) reportedly in excellent condition

As time progressed, additional cracking failures started to occur, typically after three to nine or ten years of service. Understandably, most of these cannot be referenced. Some occurred in exposed pond fPP liners by SCG and local RCP. Some SCG failures occurred in potable water reservoir fPP-R floating covers and bottom liners, in potable water tank fPP-R liners, and in aquaculture ponds. However, after four years of weathering and then ten years of production service, including withstanding 150 km/h winds, a 6 ha green fPP-R exposed geomembrane cap (EGC) cover is still working very well and is about to be permitted for another ten years of service. On the other hand, another geomembrane manufacturer’s green fPP-R floating cover on a water reservoir failed by extensive cracking after only six years. Recently, a potable water tank PP liner cracked after only 3 months. And cracking has been seen in rolls when they were removed from the shipping container. Swimming pool covers have failed where they lift off the surface. Naturally, this has been, and continues to be, a significant problem for PP geomembranes. Unfortunately, the cause of cracking has not been adequately investigated, or adequately published, unlike the early stress cracking problems in HDPE geomembranes. As a consequence of the HDPE investigations HDPE formulations have been improved to essentially eliminate SC concerns in geomembranes from the major international manufacturers. However, because of a lack of causative information PP floating covers are being replaced with chlorosulfonated polyethylene (CSPE) floating covers.

Failures have occurred in PP geomembrane made by at least eight or nine manufacturers, and in all colors of material. As a consequence of these failures the Geosynthetic Institute suspended standard Specification GRI GM 18 for “Test Properties, Testing Frequency and Recommended Warrant for Flexible Polypropylene (fPP and fPP-R) Nonreinforced and Reinforced Geomembranes” in May 2004. The failing materials were meeting the standard’s weathering specifications introduced in February 2001. The GM 18 standard required an Oven Aging retained high pressure oxidative induction time (HP-OIT, ASTM D5885) of 60% for black material and 50% for other colors. For UV resistance the retained HP-OITs were 80% (black) and 60% (other colors).

Bottom liner cracks typically occur on the tops of wrinkles at floor/wall corners of tanks (Figure 1) and on any wrinkles on the floors of open ponds. Black geomembrane is often whitened along the wrinkles. The severity of cracking increases with hydrostatic head. In exposed pond liners at the tops of slopes cracks occur, as they did in HDPE liners, along the edges of extrusion welds (in the lower sheet) and then diverging into the panel (Figure 2).

Figure 1. Crack on whitened wrinkle in fPP at floor/wall corner

Figure 2. Crack along edge of weld moving into panel of fPP

In floating covers cracks usually occur in the stressed regions at the tops and bottoms of the drainage troughs, at the ends of ballast tubes in the troughs, and near the tensioning tabs on tensioned covers. Rarely does cracking occur in the horizontal material floating on the water.

In fPP-R cracking usually starts along the warp reinforcing yarns as shown in Figure 3. Individual cracks above the weft yarns link up to form long cracks along the warp yarns. These cracks may form independently of the direction of the apparent primary stress. Thus, cracks at the tops of drainage troughs in floating covers do not necessarily initiate along the bend from flat surface to wall of trough (i.e. parallel to the axis of the trough) but may occur around the bend normal to the direction of the trough. Similarly, initial cracks on the reservoir side slopes may be oriented up and down the slope not across the slope. This occurs because the warp (roll direction) yarns are typically more spherical in cross section than the more oval weft (cross direction) yarns, thereby resulting in thinner and more highly stressed PP polymer above them. Cracking then starts along the weft yarns (Figure 3) until discrete squares of polymer are left above the reinforcement openings. Ultimately these squares spall away (Figure 4) leaving the reinforcing yarns exposed. The yarns then rapidly degrade leaving a fibrous tangle on the surface (Figure 5).

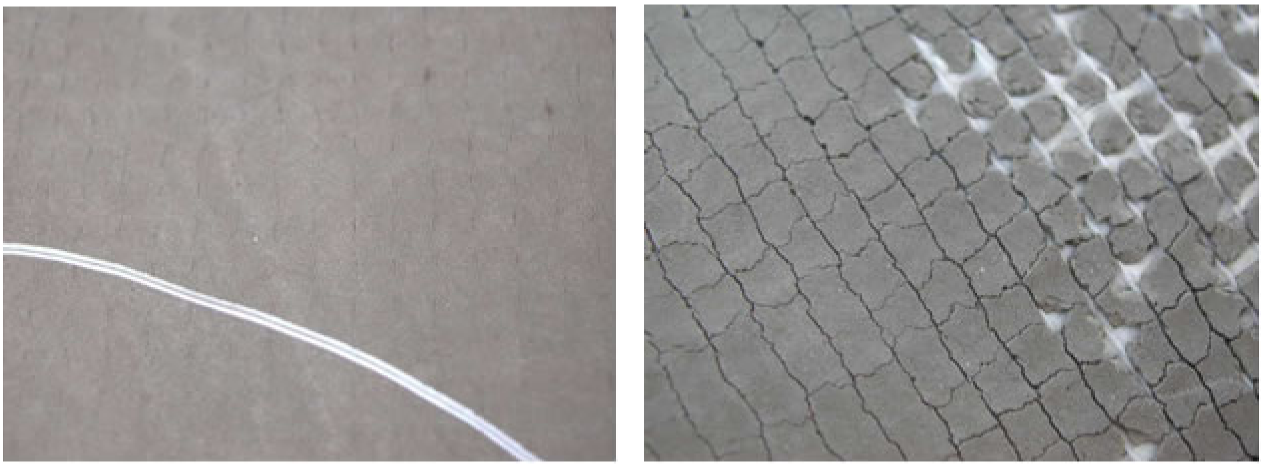

Figure 3. Initial cracking above reinforcing warp yarns (left). Subsequent cracking along weft yarns (right).

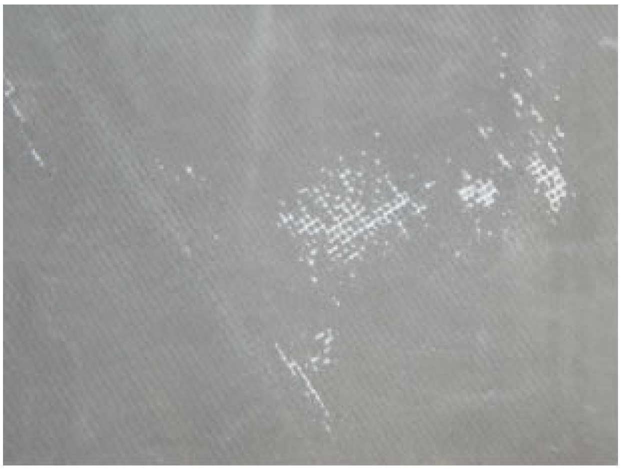

Figure 4. Squares of polymer spall away

Figure 5. Exposed reinforcement degrades

The exposed side slope liner failure in Figure 6 occurred after 9 years in a hot sunny environment. The side slope floating cover failure in Figures 3, 4, 5 and 6 occurred after 6 years in a cold winter and hot summer environment. Much of the stress in this case was caused by constant wind uplift and flapping of the excess side slope material.

Figure 6. Cracking (dark areas) in tensioned fPP-R floating cover

The cracks in Figure 7 resulted from puncture stresses imposed by the hard corners of the welded end flaps on ballast tubes. In some cases the cracks can grow to 400 mm or more. In some cases they may only penetrate to the scrim. In all cases, even though the cracks are not very large and would appear to be repairable it has been impossible to adequately clean the old surface and to thermally bond a new patch to it (Figure 8). The material is apparently quite badly oxidized. One of the most successful, but not guaranteed, methods of removing degraded material from the liner surface is a hard scrub using naptha. Alternatively, patches could be hot-air welded to the underside of the liner.

Figure 7. Short cracks (circled) at ballast tube end protrusions

Figure 8. Poorly bonded repair patch

Figure 9 shows a white fPP-R liner installed in a concrete basin potable water reservoir. Since installation the liner had been leaking. After only one year repairs were initiated but were very difficult to make. It can be noted that liner above the water line is yellowing, probably the result of oxidation. Swimming pool covers have been oxidized between where they lift off the water and the peripheral fastening.

Figure 9. Potable water reservoir liner

TESTING

It appears that accelerated oxidation is occurring in these liners and floating covers that could be the result of synergies between five factors:

- UV exposure
- thermal exposure
- water chemistry (chlorine)
- stress
- stabilizer package.

The stabilizer package in several samples taken from an fPP geomembrane which underwent the limited RCP failure shown in Figure 2 was investigated with the results shown in Table 1 (Peggs 2005).

Table 1. Antioxidant (AO) concentrations in fPP samples (%)

Component	Specification	Manufactured	Exposed
Chimassorb 944	0.2	ND - 0.02	ND - 0.21
Tinuvin 770	0.1	ND - 0.01	ND - 0.077
Tinuvin 328	0.1	ND - 0.084	ND - 0.065
Irganox 1010	0.1	Trace - 0.06	ND - 0.051
Irgafos 168	0.2	0.05 - 0.089	0.11 - 0.15

ND – not detected

It was apparent that the distribution of components was far from homogeneous. Therefore, protection would not be uniform everywhere on the surface of the geomembrane. Thus the critical combination of stress and degradation would vary across the surface. Not only is a stress required to cause a cracking failure, but the same stress will accelerate the extraction of additives (Czerny 1972). Therefore, cracking could occur on the top of one wrinkle but not on top of an adjacent, even sharper, wrinkle.

Peggs (2006) also reported the effects of stress on thermal and UV degradation rates. Archive samples of the reservoir fPP-R floating cover shown in Figure 6 were subjected to GRI GM 18 oven aging and UV resistance tests, both under a constant tensile load and without loading. Strip specimens were cut on the bias (at 45° to the reinforcing yarns) so all the stress would be taken by the polymer. HP-OITs were measured before testing and after break and are shown in Table 2. Initial breaks occurred over the warp reinforcing yarns as they did in the field. Times to break were approximately 500 h.

Table 2. HP-OITs before and after break (min and %)

	Unstressed		Stressed	
	(min)	(%)	(min)	(%)
Archive HP-OIT	133		133	
Thermal aged	130		62	
OIT retained		98		47
GRI GM18 spec.		50		-
UV exposed	102		<1	
OIT retained		77		0
GRI GM 18 spec.		60		-

It appears that stress, as expected, accelerates the thermo- and photo-oxidation degradation rates and consequently the onset of cracking. Consequently, Peggs (2006) proposed modified specifications as follows:

- Oven aging (GRI GM 18, 2002) under a stress of 1 MPa – retained HP-OIT >75%
- UV Resistance (GRI GM 18, 2002) under stress of 1 MPa – retained HP-OIT >75%

However, GRI has performed further testing on fPP geomembranes resulting in a provisionally updated (June, 2006) GRI GM 18 specification in which oven aging is not specified, but in which UV Resistance is performed for 20,000 h. Retained strength must exceed 50%, retained elongation must also exceed 50%, and there must be no visible surface cracking. GRI reportedly (Koerner 2007) has not observed any effect of stress. Neither Peggs nor GRI have performed tests in chlorinated water.

Some interesting test data have recently been generated by Mills (2008). Bent strip ASTM D1693 stress cracking tests were performed with notched fPP specimens immersed in 1% (volume) sodium hypochlorite solutions, a much higher concentration of chlorine than would be found in potable water reservoirs – typically 2 or 3 ppm. Geomembrane samples were made using a reference resin (a proprietary formulation) with zero, 2%, and 3% of additional AO (Irganox 1010). The additives were extracted and concentrations determined before exposure to hypochlorite and after 150 h bent exposure at 50°C. HP-OIT was measured on reference and exposed specimens. The results are shown in Table 3.

Table 3. fPP exposed to sodium hypochlorite solution (Mills 2008)

Sample	**Extra AO added (%)**	**1% NaOCL exposure (h)**	**Irganox 1010 (ppm)**	**HP OIT (min)**
1	0	0	1260	55
2	2	0	2020	82
3	3	0	2310	81
4	0	150	1000	23
5	2	150	1607	20
6	3	150	2320	31

Both the baseline and immersed specimens show the increasing AO as the extra AO is added. Surprisingly, the AO extracted is not significantly lower in the immersed specimens. The maximum reduction is ~20%. However, the HP-OIT retained by the immersed specimens is only ~39%. Therefore, it appears that even though the AO has not been extracted it has lost its ability to protect the PP. Mills (2008) suggests that the AO has been "deactivated", perhaps having diffused to a location in the microstructure where it is ineffective.

When commercially available geomembrane samples were tested in the same way, all HP-OITs fell to less than 5 minutes in 150 h of immersion. Mills (2008) noted that when HP-OIT decreased to ~5 minutes surface micro-cracking occurs within ~1000 h.

The author requested that an unstressed specimen be immersed by Mills (2008) in the same solution as a bent stressed specimen to observe the effect of stress. Baseline HP-OIT was 72 min. After 150 h of immersion the HP-OITs were 28 min (unstressed) and 15 min (stressed), but after 300 h they were 16 min and 14 min respectively. The implication is that stressed material does indeed initially degrade faster, and may fail faster than unstressed material, but that both end up equally degraded.

SUMMARY

The limited information available suggests that stress has a significant effect on the aging of fPP geomembranes whether under UV, thermal, or chlorinated water exposure. The practical evidence from the field is that chlorinated water is a particularly aggressive degrading environment. As such, it is probably wise to avoid chlorinated water applications of PP geomembranes unless it can be demonstrated that a resistant material is available. It may be possible to do this through simple bent strip testing.

While fPP geomembranes made by several different manufacturers have suffered cracking in water applications, the same materials have exhibited excellent performance characteristics in other weather-exposed applications.

However there are also manufacturers that have had no significant cracking problems. Wallace (2008) reports satisfactory performance of floating covers on potable water reservoirs for 5 years. There are also an increasing number of different PP resins becoming available for geomembrane manufacturing. However, these new resins will also need careful evaluation.

More research work still needs to be done to better understand the mechanisms of accelerated degradation and cracking of fPP geomembranes, but this will eventually be done, as it was for stress cracking in the early HDPE geomembranes, and fPP geomembranes will perform all the better as a result.

CONCLUSIONS

Flexible PP geomembranes in general have demonstrated both excellent and problematic weathering performance characteristics. Excellent performance has been observed in exposed geomembrane cap applications.

Poor performance, stress cracking, has been observed in potable water reservoir floating cover and liner applications. Poor performance appears to be a function of the antioxidant formulation and its distribution within the material.

Stress appears to initially accelerate the rate of degradation. Degradation and accelerated oxidation appear to be a function of the extraction or deactivation of the antioxidants.

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